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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>C08G 65/30, D21H 17/56</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/22601</b>  <b>(43) International Publication Date:</b> 23 December 1992 (23.12.92)
<b>(21) International Application Number:</b> PCT/EP92/01134 <b>(22) International Filing Date:</b> 19 May 1992 (19.05.92)  <b>(30) Priority data:</b> 91201553.4 19 June 1991 (19.06.91) EP <b>(34) Countries for which the regional or international application was filed:</b> NL et al.  <b>(71) Applicant (for all designated States except US):</b> AKZO N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GORZYNSKI, Marek [DE/DE]; Am Courtenbachshof 3, D-5160 Düren (DE). PINGEL, Andreas [DE/DE]; Aachener Strasse 3, D-5160 Düren (DE).		<b>(74) Agent:</b> SCHALKWIJK, Pieter, Cornelis; Akzo N.V., Velperweg 76, Postbus 9300, NL-6800 SB Arnhem (NL).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), PL, RU, SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> EPIHALOHYDRIN-BASED RESINS HAVING A REDUCED HALOGEN CONTENT  <b>(57) Abstract</b>  The disclosed invention pertains to a process for the preparation of a water-soluble, nitrogen-containing, epihalohydrin-based resin having a reduced content of total halogen, organic halogen, adsorbable organic halogen (AOX) and by-products. The process involves treatment of nitrogen-containing, epihalohydrin-based resins or intermediate reaction-products with a basic ion-exchanger. The invention also pertains to novel resins displaying such halogen contents far below the values known in the art. Subject resins are useful as wet-strength agents for paper and are preferably of the polyaminoamide-epihalohydrin type.		

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## EPIHALOHYDRIN-BASED RESINS HAVING A REDUCED HALOGEN CONTENT

The invention pertains to a process for the preparation of a water-soluble, nitrogen-containing, epihalohydrin-based resin comprising the  
5 step of subjecting the resin to an organic halogen reducing after-treatment.

Resins of the above type, mainly polyaminoamide-epihalohydrin resins, are well-known and find wide usage as wet-strength agents for paper.  
10 Epihalohydrin is known to impart wet-strength efficacy to polyaminoamides, but also causes the eventual resins to contain large amounts of organic halogen. A significant number of efforts to overcome this problem while retaining the product's wet-strength imparting effect has been reported.

15 Thus, a process of the type mentioned in the opening paragraph, which can be based on conventional previous reaction steps, e.g. comprising the reaction of polyaminoamide and epihalohydrin, is known from published European Patent Application No. 0 349 935. Said step  
20 consists of contacting the prepared resin with a base to convert it into a product having a pH >8, after which neutralization can take place. In this manner the organic chlorine content can be reduced to as little as 1% by weight. However, it is disclosed that, irrespective of the extent of the reduction of the organic chlorine content, the  
25 total chlorine content will remain unchanged. This is a serious limitation of the effect of the after-treatment, the remaining inorganic chlorine being a potential source of newly formed organic chlorine since it is the aqueous resin solution in which a new equilibrium will be established.

30 The invention has for one of its objects to obviate this drawback by providing a method for reducing the total chlorine content. Also, the invention meets the objective of further reducing the content of organic halogen without the resin's favourable properties being adversely affected.

5 In order to meet these and other objectives, the invention consists in that in a process of the above-described known type the after-treatment comprises contacting the resin with a basic ion-exchanger.

10 Unexpectedly, the after-treatment according to the present invention results in the resin subjected to it having a surprisingly low total halogen content of 1% by weight or lower, calculated on solid resin. It should be noted that in EP 369 935 the total halogen content remains at a level of 13,52% by weight, calculated on solid resin. So, clearly, the process according to the invention results in an unobvious improvement, further evidenced by the fact that the total halogen content in the novel resins prepared in accordance with the invention is even lower than the organic halogen content of the known resins.

20 Evidently, the total halogen content of the resins prepared in accordance with the present invention being considerably lower than in known resins, the resulting organic halogen content is lower also, viz. below 0,1% by weight, calculated on solid resin. In this respect it should be noted that the following art-recognized definitions of halogen contents apply to the description of subject invention:

- 25 - Total halogen content obviously indicates all halogen present and this is the sum of all organic and inorganic halogen present.
- Organic halogen content indicates all halogen linked to organic molecules, i.e. total halogen minus inorganic halide ions.
- 30 - Adsorbable organic halogen, hereinafter referred to as AOX, is a term widely used in the art of wet-strength agents for paper. It indicates all organic halogen that can be determined by means of adsorption onto activated carbon using the method according to DIN 38409, part 14.

- By-products content refers to 1,3-dihalo-2-propanol (DXP) and 1-halo-2,3-propane diol (MXP), which are the most important undesired by-products formed when a resin is prepared from a reaction mixture containing epihalohydrin. Since the most common epihalohydrin in the art is epichlorohydrin, by-products content frequently indicates DCP (dichloro propanol) and MCP (mono chloro propane diol).

A different approach towards low halogen contents is followed in EP 335 158, which discloses substitution of epihalohydrin by halogen-free crosslinkers. The crosslinker being allowed to contain a maximum of 15 mole % epihalohydrin, the resin is not an epihalohydrin-based resin in accordance with the present invention. Particularly low halogen values are disclosed if no epihalohydrin is present at all.

Several other processes for the preparation of water-soluble, nitrogen-containing, epihalohydrin-based resins with reduced halogen contents have been reported, but the halogen contents of the resins prepared by the disclosed processes by no means approximate the low level of the novel resins prepared in accordance with the present invention.

EP 282 862, which discloses a process of the type mentioned in the opening paragraph in which the after-treatment consists of reacting the epihalohydrin-based reaction products with a base followed by conversion with halogen-free acids, presents an organic halogen content of 2,73% by weight, calculated on solid resin. EP 332 967, which discloses a process similar to the EP 282 862 process but in which essentially a mixture of polyamines is applied, presents an organic halogen content of 0,74%, calculated on solid resin. Another disclosure, EP 374 938, only demonstrates a reduced by-product content when referring to organic halogen. The products prepared in accordance with the present invention not only display unexpectedly low total and

organic halogen contents, but also unexpectedly low AOX and by-products contents.

5 It is noted that basic ion-exchangers are known to remove inorganic halide ions. It should be stressed that this does not at all suggest their aiding in the removal of organic halogen, let alone the present finding which provides a significant reduction of total halogen, organic halogen, AOX, and by-products contents and thus presents a  
10 solution to a serious problem in the art. The nature of the frequently complicated processes disclosed, which typically includes the alteration of several process parameters, does not at all suggest that a relatively simple after-treatment as applied in accordance with the present invention would have such an impact on the total halogen content, let alone the organic halogen, AOX, and by-products contents.  
15 The after-treatment, which in itself can be carried out in a simple manner, generally results in novel products having a total halogen content of below 1% by weight, an organic halogen content of below 0,1% by weight, an AOX content of below 0,002% by weight and by-product contents of below 0,025% by weight of DXP and 0,005% by weight  
20 of MXP, calculated on solid resin.

In order to perform the process of the present invention it is a requirement to use a basic, preferably strongly basic ion-exchanger.  
25 Ion-exchangers are known in the art and can generally be described as solid substances which upon contact with an electrolyte solution are capable of taking up ions (either positive or negative) and exchange these for an equivalent amount of different ions bearing the same sign. Though the invention process is not limited with respect to the  
30 specific type of ion-exchanger used, the most important class of materials is formed by ion-exchanger resins, more specifically synthetic resins. Ion-exchangers of this kind generally comprise a high polymer network of hydrocarbon chains that acts as a matrix for charge-carrying groups linked to it. Basic ion-exchangers generally

carry cationic groups such as  $-NH_3^+$ ,  $=NH_2^+$ ,  $=N^+$ ,  $-S^+$ . Ion-exchanger resins can be regarded as polyelectrolytes that, due to their crosslinked matrix structure, swell in water rather than dissolve. Since ion-exchangers belong to the common knowledge of the skilled artisan, a detailed explanation need not be given here. Reference is made to Ullmann, Encyclopädie der Technischen Chemie, which has a chapter on ion-exchangers (in the 1957 edition this is Volume 8, pages 787 ff.). Good examples of basic ion-exchangers that can be used in the process of the present invention include those listed in the table given by Ullmann (above edition, page 817). Other basic ion-exchangers, e.g. those based on a polystyrene or polyacrylic matrix, are equally suitable, and admixed resins can also be applied.

Preferably, the ion-exchangers used in the process of the present invention contain tertiary amino and/or quaternary ammonium groups. Strongly basic ion-exchangers are greatly preferred over weakly basic ion-exchangers. Good examples of such ion-exchangers include resins carrying quaternary ammonium groups having three lower alkyl substituents or quaternary ammonium groups containing at least one lower alcohol substituent. Mixed resins can also be applied. The highest preference is given to ion-exchanger resins of a type carrying quaternary ammonium substituents selected from the group consisting of trimethyl ammonium, dimethylethanol ammonium, and mixtures thereof. Applying these most preferred strongly basic ion-exchangers results in epihalohydrin-based resins having a total halogen content of below 0,5% by weight and an organic chlorine content of below 0,05%, calculated on solid resin. It has been possible to reduce the AOX content to even below 0,0005% by weight and to reduce the by-products content to below 0,005% by weight of DXP and 0,003% by weight of MXP.

A detailed, unlimitative description of the after-treatment in accordance with the present invention typically is as follows:

- the ion-exchanger resin to be used is transferred from the chloride form (as it is frequently available) to the hydroxy form (regeneration) and washed
- 5 - mixing with regenerant is continued until regeneration is completed
- a solution of epihalohydrin-based resin (up to 20% solids content) is passed through the exchanger resin bed, after which the  
10 exchanger resin is washed.

15 A typical dwell time for the epihalohydrin resin to be in contact with the ion-exchanger bed generally is of the order of about 2 hours, but dwell times of less than 1 hour are preferred.

20 The after-treatment in accordance with the present invention can basically be preceded by any known process for the preparation of epihalohydrin-based resins. Such processes include those disclosed in the above-referenced European Patent Applications, which are all incorporated by reference for all purposes. Further disclosures of processes for the preparation of water-soluble, nitrogen-containing, epihalohydrin-based resins are found in EP 74 558, U.S. 3 311 594, U.S. 4 336 835, U.S. 3 891 589, and U.S. 2 926 154, which are all  
25 incorporated by reference for all purposes. The process according to the present invention may also comprise subjecting commercially or otherwise readily available epihalohydrin-based resins to the after-treatment described hereinbefore. A more detailed description of typical examples of epihalohydrin-based resins will follow below, after a discussion of the novel products to which the invention also  
30 pertains.

The invention pertains also to novel, water-soluble, nitrogen-containing, epihalohydrin-based resins obtainable by the above

described process. The novel resins fulfill the requirement of having reduced AOX and by-products contents and are characterized by having a total halogen content of below 1% by weight, calculated on solid resin. As is also clear from the above, these novel resins constitute a surprising and unexpected finding, since in view of EP 349 935 the artisan would not expect an epihalohydrin-based resin with a total halogen content even lower than the disclosed organic halogen content to be obtainable. In a preferred embodiment, the invention pertains to resins obtainable by a process involving the after-treatment described hereinbefore which display a total halogen content of below 0,5% by weight, calculated on solid resin.

The total halogen content for the invention resins being considerably lower than in known resins, the organic halogen content is lower also. In this respect the invention also pertains to novel resins having the unobviously low content of below 0,1% by weight of organic chlorine, calculated on solid resin. Even further preferred invention resins are obtainable, viz. those displaying an organic halogen content of below 0,05% by weight, calculated on solid resin. As is clear from the earlier-discussed disclosures of epihalohydrin-based resins with reduced halogen contents, the invention resins cannot be derived from the art in view of their low contents of total chlorine, organic chlorine, AOX and by-products. In this respect the invention also pertains to epihalohydrin-based resins displaying an AOX content of below 0,01% by weight and by-product contents of below 0,005% by weight of DXP and 0,003% by weight of MXP, calculated on solid resin. Preferred resins are obtainable in which the AOX content is below 0,0005% by weight, calculated on solid resin.

Subject water-soluble, nitrogen-containing, epihalohydrin-based resins which are characterized by their novel low halogen contents and are obtainable by the novel process described hereinbefore, can basically be of any type known in the art of paper wet-strength agents. In

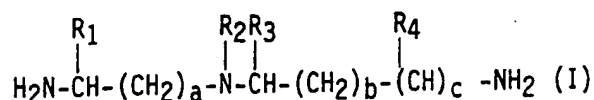
addition to the above-referenced and incorporated disclosures, preferred resins can be as follows.

5 Subject resins, also referred to as cationic thermosetting resins, generally comprise a nitrogen-containing precursor and a halogen-containing crosslinker. The resins according to the invention preferably are of the type commonly referred to as polyaminoamide-epihalohydrin resins. Epihalohydrins used in preparing such resins  
10 include, particularly, epibromohydrin and - preferably - epichlorohydrin. A typically preferred mole ratio is 1,3 - 0,7 moles of epihalohydrin per mole of basic nitrogen in the polyaminoamide. The epihalohydrin is generally comprised in the crosslinker. In preferred epihalohydrin-based resins at least a substantial part of the  
15 crosslinker is epihalohydrin, while more preferably epihalohydrin is a major part thereof, particularly about 50 to 100 mole %. It is highly preferred that the crosslinker consist of more than 80 mole % epihalohydrin.

20 The basic ingredient for the preferred resins is the polyaminoamide reaction product of a polycarboxylic, usually dicarboxylic acid and a polyamine. Suitable polycarboxylic acids include aliphatic, saturated or unsaturated, or aromatic dicarboxylic acids. Preferably, the polycarboxylic acids contain less than 10 carbon atoms. For the  
25 purpose of the invention, the term "carboxylic acid" is meant to include carboxylic derivatives also, such as anhydrides, esters or half esters.

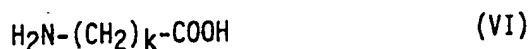
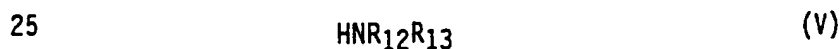
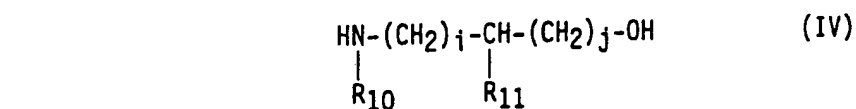
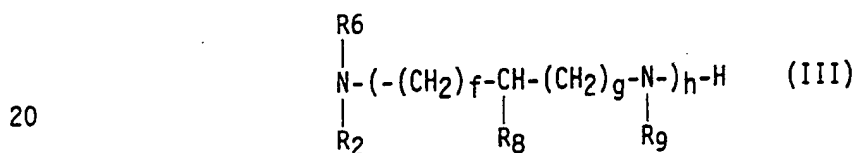
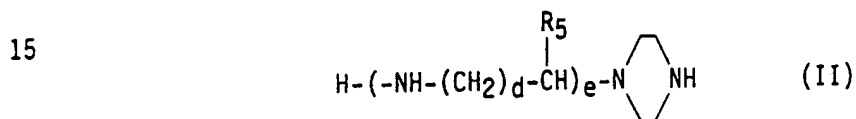
30 Suitable polycarboxylic acids and derivatives include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, and sebacic acid. Mixtures of these acids can also be applied. The preferred polycarboxylic acid is adipic acid.

Suitable polyamines include polyalkylene polyamines, or mixtures thereof, satisfying the following formula:



5 in which R<sub>1</sub>-R<sub>4</sub> represent hydrogen or lower alkyl, preferably up to C<sub>3</sub> and a-c represent integers from 0-4. Preferred polyalkylene polyamines include diethylene triamine, triethylene tetra amine, tetraethylene penta amine, dipropylene triamine, and mixtures of these amines.

10 The polyamines of formula I can very well be combined with other polyamines or mixtures of other amines. Preferably, these amines satisfy the following formulae II-VII.



30 in which R<sub>5</sub>-R<sub>13</sub> represent hydrogen or lower alkyl, preferably up to C<sub>3</sub>, d-k represent integers from 0 to 4, and l represents an integer from 1 to 5.

The polycarboxylic acid and the polyamine typically are applied in a mole ratio of from 1:0,7 to 1:1,5.

5 A water-soluble, nitrogen-containing, epihalohydrin-based resin is generally prepared from a polyaminoamide solution. The solution preferably is aqueous and can be formed of pure water or of water in admixture with a water-miscible solvent, such as ethanol or dimethyl formamide. Many different ways of performing the reaction of epihalohydrin with polyaminoamide have been described, among others in the disclosures previously incorporated hereinto. So, reaction temperatures can be either low or high and various temperature profiles can be applied. Also, reactant concentrations may vary within a broad range. Preferably, the reaction is carried out in such a way that the end-product viscosity at 20°C for a 10% solids content solution is in the range of 10-20 mPa.s, more preferably about 15 mPa.s. If 30% solids content solutions are prepared, the viscosity at 15 20°C preferably is in the range of 150-250 mPa.s, more preferably about 200 mPa.s. The resulting molecular weights may be as low as 2000, but preferably are in the range of from 100 000-1 000 000 or higher.

20 The resins according to the present invention are preferably obtained by first subjecting the epihalohydrin-based, nitrogen-containing resins to the ion-exchanger treatment described hereinbefore, and then neutralizing with acid to obtain a product having a pH of, preferably, lower than 5. More preferably, the pH is adjusted to a value between 25 about 3 and about 4.5. Resins having such preferred pH values display a better stability upon storage. It is also possible to first neutralize and then conduct the after-treatment according to the present invention. Neutralization may take place in any manner known in the art, applying any feasible inorganic or organic acids. 30 Preferred organic acids include formic acid and citric acid, whereas preferred inorganic acids include sulfuric acid and phosphorous acid. Mixtures of acids can be applied as well.

As indicated above, the resins according to the present invention can also be obtained by subjecting commercially available water-soluble, nitrogen-containing, epihalohydrin-based resins to the ion-exchanger treatment, by virtue of which novel resins are obtained which have a halogen content reduced by 95% or more.

It should be noted that, though the ion-exchanger treatment is referred to as an after-treatment, it can also be applied during preparation of the water-soluble, nitrogen-containing, epihalohydrin-based resin. In this respect a preferred embodiment of the present invention resides in a resin obtained by a two-stage process. Such a process is basically known from previously incorporated U.S. 3 891 589. The ion-exchanger treatment can be applied after either the first or the second stage. A further preferred process can be described as a three-stage reaction in the following manner:

- (a) reacting a polyalkylene polyamine of type I described hereinbefore, optionally in admixture with a polyamine of type II-VII described hereinbefore, with a dicarboxylic acid, preferably an aliphatic dicarboxylic acid, to form a polyaminoamide (PAIM);
- (b) reacting the PAIM formed under (a) with an epihalohydrin (EHH) at a temperature of below about 40°C to form a PAIM/EHH adduct;
- (c) subjecting the adduct formed under (b) to a temperature in the range of from 50 to 70°C to effect ring-closure and to obtain a precursor resin at a low degree of crosslinking;
- (d) subjecting the precursor resin formed under (c) to treatment with a basic ion-exchanger to obtain a substantially halogen-free intermediate;

(e) keeping the intermediate obtained under (d) at alkaline pH and subjecting it to a temperature below 40°C in order to form a water-soluble, nitrogen-containing, epihalohydrin-based resin;

5

(f) adjusting the pH to neutral or slightly acidic.

10 The temperature requirements given above should not be interpreted in a too strict sense. The quintessence of the three-stage process is that full crosslinking does not occur until after the removal of halogen. By virtue of the alkaline pH after the ion-exchanger treatment the intermediate obtained under (d) will be subject to crosslinking at relatively low temperatures. Of course, one can also  
15 lower the pH and consequently carry out crosslinking at a higher temperature. The resins thus prepared display the lowest levels of total halogen, organic halogen, AOX, and by-products. It is not excluded that halogen-containing by-products can be removed entirely, but this cannot be definitely concluded on the basis of the current detection methods.

20

The novel resins according to the present invention are useful as wet-strength agents for paper. As such, they have the advantage of avoiding the halogen and halogen-containing by-products contamination normally associated with using epihalohydrin-based resins in paper  
25 mills, while retaining their good wet-strength imparting properties. Hence the invention also pertains to the use of the resins described hereinbefore as wet-strength agents for paper.

30

The invention will be further illustrated hereinafter with reference to the Examples. The following Examples should be construed to be explanatory rather than limitative.

Example 1

5 A 20% solids content aqueous solution of commercially available nitrogen-containing, epichlorohydrin-based resin EtadurinNXH (ex Akzo Chemicals) was treated with basic ion-exchanger DowexSAR (ex Dow Chemical Co.) by elution over a column, and then adjusted to a pH of 3,4 with formic acid. The data measured on the old and the novel product is outlined in Table I below.

10

TABLE I

Wt% (chlorine data calculated on solid resin)

15

	DCP	MCP	AOX	Total Chlorine
old	1,5%	0,5%	2,5%	11.7%
20 novel	<0,025%	<0,005%	<0,01%	<1%
reduction by	98%	99%	99%	>90%

25

Example 2

30 Analogously to Example 1 aqueous 15% solutions of commercially available, nitrogen-containing, epichlorohydrin-based resins were treated with basic ion-exchanger. The resins treated were Nadvin®LTN-A (ex Bayer), Giluton®1100/28 and Kymene®SLX. The results were as favourable as in Example 1 and are listed in Table II.

TABLE II

5 Wt% (chlorine data calculated on product as such, the solids content being indicated below)

10 Product	Solids%	DCP	MCP	AOX Total Chlorine	
Kymene	12.8%	<0.1%	<0.1%	not det.	not det.
	treated 11.8%	13 ppm	104 ppm	6.2 mg/l	0.033%
15 Nadavin	22.4%	0.34%	0.2%	6.2 g/l	2.9%
	treated 10.7%	24 ppm	66 ppm	110 mg/l	0.19%
20 Giluton	13.7%	<0.1%	<0.1%	0.71 g/l	1.61%
	treated 16.9%	29 ppm	186 ppm	39 mg/l	0.1%

### Example 3

25 A polyaminoamide-epichlorohydrin-based resin was prepared by a two-stage process in accordance with U.S. 3 891 589, employing dimethylene triamine in admixture with N-aminoethyl piperazine as the polyalkylene polyamine starting compound and employing epichlorohydrin as the epihalohydrin starting compound. After the first reaction stage, 30 conducted at a temperature of about 20°C to about 40°C, followed by about 1 to 2 hours at 60°-70°C, the precursor resin thus obtained was cooled to room temperature and subjected to treatment with the basic ion-exchanger of Example 1. The substantially halogen-free intermediate, after coming off the ion-exchanger, was subjected to a

temperature of about 20° to about 30°C, while alkaline pH was maintained until crosslinking was complete. Thereafter, the pH of the reaction product was adjusted to 3,6, using formic acid.

5

The following data was determined, calculated on solid resin:

DCP 0,003% by weight

MCP < 0,003% by weight

AOX < 0,0003% by weight

10 Total Cl about 0,18% by weight

Example 4

Analogously to Example 1, approx. 20% solution of commercially available, nitrogen-containing epihalohydrin-based resin Etadurin H<sup>®</sup> was treated with resin ion-exchanger. Analytical results are quoted in Table III.

15

TABLE III

20

	DCP	MCP	AOX	Total Chlorine
Etadurin H (19.5%)	630 ppm	330 ppm	2,2 g/l	2,5%
Ion exchanger treated Etadurin (13.3%)	12 ppm	23 ppm	2,4 mg/l	0,056 g/l
Reduction by	98 %	91 %	>99.5 %	98 %

30

Example 5

5 A polyaminoamide-epichlorohydrin-based resin was prepared by a two-stage process in accordance with US 3.194.427, employing diethylenetriamine as polyalkylenepolyamine, adipic acid as dicarboxylic acid, and epichlorohydrin as the epihalohydrin starting compound. After the first stage (molar ratio diethylenetriamine:adipic acid = 1:1), which was performed in analogy to Example 1, the  
10 polyamide solution was treated with epichlorohydrin in analogy to Example 2 (molar ratio PAIM/ECH 1:1.20). Before HCl addition and pH adjusting the product which was cooled down to a temperature below 20°C was subject to treatment with the basic ion-exchanger of Example 1. The substantially halogen-free intermediate, after coming off the  
15 ion exchanger, was subject to treatment at a temperature of about 20°C to about 30°C, while alkaline pH was maintained until cross-linking was complete. Thereafter the pH of the reaction product was adjusted to 3,6 using formic/sulfuric acid/1:3.

20 The following data was determined and calculated on solid resin.

DCP 0.003 % by weight

MCP <0.003 % by weight

AOX <0.01 % by weight

25 Total Cl about 0.18 % by weight

Example 6

30 A few market products, such as Etadurin H® Akzo, Kymene SLX® Hercules, Giluton 1100/28 N® Giuliani and Nadavin LT-A® Bayer, were treated with ionic exchanger as in Example 1.

The following procedure was employed in order to demonstrate that the treatment of commercially available wet-strength agents with ion

exchangers does not have a significant influence on the wet-strength efficacy of these products.

5 Test sheets of approximately 70 g/cm<sup>2</sup> were prepared on a pilot paper machine (speed 2 m/min, capacity 2 kg/h). Furnish consisted of a 30/35/35 blend of bleached pine sulfate / birch sulfate / beech sulfite which had been beaten to a Schopper-Riegler freeness of 26°SR. The fillers DX40 (Omya) and clay (Koalin B) each in 5 wt% were  
10 added to the stock at a temperature of 25°C. Ther wet-strength agents were fed into the paper machine after the stock dilution. The stock consistency at the headbox amounted to 0.3% and pH remained in the range of 7.2 - 7.8 for all products and concentrations, and was not adjusted. The temperatures of the cylinders in the drying section were  
15 adjusted to 60°/80°/90°/110°C.

The paper was cured for 30 min at 100°C and then conditioned at 23°C and relative humidity of 50% (55%) for 2 h before testing. Paper strips were soaked for 5 min at 23°C in distilled water before  
20 breaking length determination on an ALWETRON TH1<sup>®</sup> Gockel & Co. GmbH Munich, hydrodynamic tester.

The results of the tests are tabulated in Table IV. The wet-strength efficacy of the ion-exchanger treated resins is expressed as a  
25 relative wet-strength efficacy in % of the breaking length of the original resins, i.e. resins not treated with ionic exchanger.

TABLE IV

5

Breaking length efficiency =  $\frac{\text{breaking-length of treated resin}}{\text{breaking length untreated resin}} \cdot 100\%$

10

Dosage [%] based  
on dry content

Etadurin H

Kymene SLX

Giluton  
1100/28sample  
example 4

15

0,3

93

92

86

98

0,6

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## Claims:

- 5 1. A process for the preparation of a water-soluble, nitrogen-containing, epihalohydrin-based resin comprising the step of subjecting the resin to an organic halogen reducing after-treatment, characterized in that the after-treatment comprises contacting the resin with a basic ion-exchanger.
- 10 2. A process according to claim 1, characterized in that the basic ion-exchanger is a synthetic resin containing strongly basic substituents selected from the group consisting of tertiary amino groups, quaternary ammonium groups, and mixtures thereof.
- 15 3. A process according to claim 2, characterized in that the strongly basic substituents are selected from the group consisting of trimethyl ammonium, dimethyl ethanol ammonium, and mixtures thereof.
- 20 4. A process for the preparation of a water-soluble, nitrogen-containing, epihalohydrin-based resin comprising a first stage in which a polyaminoamide is reacted with an epihalohydrin to form an intermediate which has not reached a stage of complete crosslinking and a second stage in which complete crosslinking occurs, characterized in that after the first stage the intermediate is
- 25 contacted with a basic ion-exchanger.
- 30 5. A water-soluble, nitrogen-containing, epihalohydrin-based resin having a reduced organic halogen content, characterized in that it has a total halogen content of below 1% by weight, calculated on solid resin.

6. A resin according to claim 5, characterized in that the total halogen content is below 0,5% by weight, calculated on solid resin.
- 5 7. A resin according to claim 5, characterized in that the organic halogen content is below 0,1% by weight, calculated on solid resin.
- 10 8. A resin according to claim 7, characterized in that the organic halogen content is below 0,05% by weight, calculated on solid resin.
- 15 9. A water-soluble, nitrogen-containing, epihalohydrin-based resin having a reduced adsorbable organic halogen (AOX) content, characterized in that the AOX content is below 0,01% by weight, calculated on solid resin.
- 20 10. A resin according to claim 9, characterized in that the AOX content is below 0,0005% by weight, calculated on solid resin.
- 25 11. A water-soluble, nitrogen-containing, epihalohydrin-based resin having a reduced by-products content, characterized in that 1,3-dihalo-2-propanol (DXP) is present in an amount of below 0,1%, calculated on solid resin and monohalo propane diol (MXP) is present in an amount of below 0,05%, calculated on solid resin.
- 30 12. A resin according to claim 11, characterized in that DXP is present in an amount of below 0,005% by weight and MXP is present in an amount of below 0,003% by weight, both calculated on solid resin.
13. The use of a resin prepared in accordance with any one of the claims 1-4 as a wet-strength agent for paper.

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14. The use of a resin according to any one of the claims 5-12 as a wet-strength agent for paper.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/01134

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08G65/30; D21H17/56		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08G ; D21H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	EP,A,0 349 935 (HOECHST AG) 10 January 1990 cited in the application see page 3, line 3 - line 8; claims 1,4,13; examples; tables 1,2 ---	5-14
A	EP,A,0 282 862 (BAYER AG) 21 September 1988 cited in the application see page 6, line 13 - line 27; examples ---	5-14
A	EP,A,0 332 967 (BAYER AG) 20 September 1989 cited in the application see examples ---	5-14
A	EP,A,0 374 938 (SUMITOMO CHEMICAL CO.) 27 June 1990 cited in the application see claim 1; examples --- -/-	1,5-14
<p><sup>10</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
01 SEPTEMBER 1992	14. 09. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BOEKER R.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 994 627 (M.CUSCURIDA ET AL.) 19 February 1991 see claim 1  ---	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9201134  
SA 61214

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0349935	10-01-90	DE-A- 3822490 US-A- 5019606	04-01-90 28-05-91
EP-A-0282862	21-09-88	DE-A- 3708544 DE-A- 3866901 JP-A- 1229027 US-A- 4857586	29-09-88 30-01-92 12-09-89 15-08-89
EP-A-0332967	20-09-89	DE-A- 3808741 JP-A- 2006530 US-A- 4975499	28-09-89 10-01-90 04-12-90
EP-A-0374938	27-06-90	JP-A- 2170825 US-A- 5017642	02-07-90 21-05-91
US-A-4994627	19-02-91	None	

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International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>D21H 17/55</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/21384</b>  <b>(43) International Publication Date:</b> 28 October 1993 (28.10.93)
<b>(21) International Application Number:</b> PCT/US93/03431 <b>(22) International Filing Date:</b> 12 April 1993 (12.04.93)  <b>(30) Priority data:</b> 07/868,321 14 April 1992 (14.04.92) US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventor:</b> AMEY, Ronald, Lee ; 17 Woodward Drive, Wilmington, DE 19808 (US).  <b>(74) Agents:</b> HANDLEY, Earl, L. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> CA, FI, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR THE MANUFACTURE OF AN AQUEOUS SOLUTION OF POLYAMIDE-EPICHLOROHYDRIN RESIN HAVING LOW LEVELS OF FREE EPICHLOROHYDRIN AND RELATED HYDROLYSIS PRODUCTS  <b>(57) Abstract</b>  A process for lowering the amount of epichlorohydrin and related hydrolysis compounds contained in paper strength enhancing resins by treating an aqueous solution of the resin with an adsorbent.		

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FI	Finland				

# TITLE

PROCESS FOR THE MANUFACTURE OF AN AQUEOUS SOLUTION  
OF POLYAMIDE-EPICHLOROHYDRIN RESIN HAVING LOW LEVELS OF  
FREE EPICHLOROHYDRIN AND RELATED HYDROLYSIS PRODUCTS

## FIELD OF THE INVENTION

This invention relates to the manufacture of an aqueous solution of polyamide-epichlorohydrin resin having low levels of epichloro-hydrin and related hydrolysis products, and to paper treated with such solutions. Paper so treated has improved wet and dry strength over paper that has been treated with polyamide-epichlorohydrin resin solutions that have higher amounts of free epichlorohydrin and related hydrolysis products. Furthermore, the paper product treated with aqueous solutions having low levels of free epichlorohydrin and related hydrolysis products contains smaller amounts of these chemicals that are suspected of being carcinogens and are environmental pollutants.

## BACKGROUND OF THE INVENTION

Paper strengthening resins are sold commercially as aqueous solutions. Commonly such resins are thermosetting, polymeric reaction products of epichlorohydrin and a polyamide derived from a polyalkylene polyamide and certain dicarboxylic acids. U.S. Patent 2,926,154 to Keim describes aqueous solutions of such resins. Typically aqueous solution of such resins contain an amine curing accelerator such as ethylenediamine or diethylenetriamine. Such compositions are disclosed in Espy U.S. Patent 3,442,754. The presence of the accelerator makes it possible to thermally set the resin in a shorter time.

Commercially such aqueous solution usually contain about 10 to 35% by weight resin. Most of the remaining portion of the solution is water.

Such commercial aqueous solutions typically contain epichlorohydrin, dichloropropanol and chloropropanediol; the latter two compounds are hydrolysis products of epichlorohydrin. These compounds are suspected carcinogens and contribute to environmental pollution during the paper making process.

A variety of references describe the removal of organohalogen compounds from water by use of various adsorbents including ion exchange resins, polymeric adsorbents, silica, alumina, clays, activated carbons, zeolites, etc. See, for example,

K. Dorfner, Ion Exchangers, Properties and Applications. (Ann Arbor Science Publishers Inc., 1972, Ann Arbor);

Ion Exchangers, K. Dorfner, Ed. (Walter de Gruyter, NY, 1991);

-2-

Amberlite® Product and Technical Bulletin, for Amberlite® IRA-93 ion exchange resin, Rohm and Haas Co., 1981.

### SUMMARY OF THE INVENTION

The present invention is a process for lowering the amount of epichlorohydrin and related hydrolysis compounds that are contained in an aqueous solution of polyamide-epichlorohydrin resin, which comprises adsorbing epichlorohydrin and related hydrolysis compounds contained in an aqueous solution of polyamide-epichlorohydrin resin by contacting the aqueous solution with an adsorbent selected from the group consisting of ion exchange resins, activated carbon, zeolites, silica, clays, and alumina.

The present invention also is a process for increasing the strength of paper and lowering the amount of epichlorohydrin and related hydrolysis compounds in paper containing polyamide-epichlorohydrin strength-enhancing resin, which comprises adsorbing epichlorohydrin and related hydrolysis compounds contained in an aqueous solution of polyamide-epichlorohydrin resin by contacting the aqueous solution with an adsorbent selected from the group consisting of ion exchange resins, non-ionic polymeric resins, synthetic carbonaceous adsorbents, activated carbon, zeolites, silica, clays, and alumina, and then using the resulting solution as an additive in the manufacture of paper products. The resulting solution may be added to pulp as it is being fabricated into paper, or the resulting solution may be used to impregnate paper that has already been fabricated.

### DETAILED DESCRIPTION

The process for forming the starting material for the present invention, i.e., the aqueous solution of polyamide-epichlorohydrin, is well-known and is described in Keim U.S. Patent 2,926,154. As pointed out in this patent the polyamide portion of the resin is the reaction product of a polyalkylene polyamide having two primary amine groups and at least one secondary amine group with a saturated aliphatic dicarboxylic acid. Suitable polyamines include polyethylene polyamine, polypropylene polyamine, polybutylene polyamine, etc. Suitable saturated dicarboxylic aliphatic acids are preferably those containing 3 to 6 carbon atoms, for example, malonic, succinic, glutaric and adipic.

The Keim patent also teaches reaction conditions and the preferred concentration of ingredients.

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In the examples below Cascamid® C-12, a polyamide-epichlorohydrin resin produced by Borden Inc., was the wet strength resin treated.

The levels of epichlorohydrin, dichloropropanol and chloropropanediol were measured by capillary gas chromatography using calibrated standards.

The wet and dry strength of paper was measured on unbleached kraft paper that had been treated with an aqueous solution of 0.1% resin which was applied by a size press. 4 inch by 1 inch strips of treated paper were re-wetted in distilled water by soaking for 1 hr., lightly blotted to remove excess water and then tested in a tensile strength instrument. Wet strength is reported in pounds required to break the test sample per inch of sample width. Dry strength is similarly measured for treated sample which has not been re-wetted. Wet-to-dry strength ratio is reported as percent.

The adsorbent beds are prepared by slurring the adsorbent with deionized water, transferring the slurry to a column containing deionized water, and allowing the water to slowly drain from the column until the top surface of the bed is just covered with water and a packed bed free of entrained air created. The bed is further backwashed with deionized water to remove air bubbles and to classify the adsorbent particles within the bed. Basic ion exchange resin particles are previously washed with sodium hydroxide followed by washing with deionized water to insure that resin particles are in the desired hydroxide form. Adsorbents such as activated carbon with contain extremely fine particles should be repeatedly decanted at the aqueous slurry stage to remove such fine particles which can cause plugging of the bed. Adsorbents beds can be regenerated by using a wash appropriate to the adsorbent which removes adsorbed epichlorohydrin and hydrolysis products. The polyamide-epichlorohydrin solution can be fed to the bed by gravity or by a pump. The polyamide-epichlorohydrin solution can be contacted with the adsorbent at temperatures from about 0 degrees C to about 50 degrees C. (Lower temperatures limit the solution pumpability and higher temperatures cause undesirable loss of polyamide-epichlorohydrin resin properties.) Pumping pressures are limited by the particular adsorbent selected by the physical limitations of the pump and column construction. Bed size is very highly dependent on the particular specific adsorption capacity of the adsorbent bed, the level of epichlorohydrin and its hydrolysis products in the solution being treated polyamide-epichlorohydrin solution, and the level of epichlorohydrin and its hydrolysis products desired in the treated, effluent polyamide-epichlorohydrin solution.

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Pumping flow rates for the polyamide-epichlorohydrin solution are dependent on the specific adsorbent chosen but typically range from 1 to 40 bed volumes/hour.

Alternatively, the polyamide-epichlorohydrin solutions can be mixed with the slurry of adsorbent, stirred to insure thorough contact with the adsorbent, and then the solution of treated polyamide-epichlorohydrin is separated from the adsorbent by filtration or decantation.

Adsorbents are selected from the group consisting of ion-exchange resins, non-ionic polymeric resin, synthetic carbonaceous adsorbents, activated carbon, zeolites, silica, clays, and alumina. Preferred adsorbents are selected from the group consisting of weakly basic ion exchange resins, non-ionic macroporous polymeric resins, and synthetic carbonaceous adsorbents. Most preferred adsorbents are selected from the group consisting of synthetic carbonaceous adsorbents.

Examples of such adsorbents include: Amberlite® IRA 93, a weakly basic macroporous, macroreticular resin; Amberlyst® A-21, a weakly basic macroreticular resin; Amberlite® XAD-2, -4, -7, -16, a family of non-ionic macroporous polymeric resins; Amborsorb® 563 and 572, a family of synthetic carbonaceous resins; Darco® 4-12 mesh granular activated carbon; Norit® ROO.8 pelletized activated carbon; 13X molecular sieve (1/8" pellet); 5 Angstrom molecular sieve (1/8" pellet); 100-200 mesh silica; neutral alumina; basic alumina; Montmorillonite, K10 and KSF, layered clays.

#### EXAMPLES

##### Example 1

100 grams of Amberlite® IRA-93 resin was slurried with 200 ml of deionized water and periodically stirred for 1 hr. The water was decanted and the resin stirred with 200 ml of 1 Normal HCl which was then decanted. The resin was slurried with 200 ml of water, decanted; slurried with 200 ml of 0.5 Normal NaOH, decanted; slurried with 200 ml water decanted; and the entire cycle repeated. The resin was slurried and loaded to a chromatography column with a glass frit in the bottom and a stopcock. Approximately 150 ml of Cascamid® C-12 was passed through the bed. The Cascamid® contained about 5.2 ppm of epichlorohydrin, about 10,200 ppm of dichloropropanol and 105 ppm of chloropropanediol. A treated sample contained less than 1 ppm of epichlorohydrin, less than 2 ppm of dichloropropanol and about 15.5 ppm of chloropropanediol.

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Kraft paper was treated with the sample. The treated paper had a wet strength of 13.0 lb./in, a dry strength of 46.5 lb./in and a wet/dry ratio of 27.9%. A sample of kraft paper treated with the untreated Cascamid® C-12 had a wet strength of 12.5 lb./in, dry strength of 45.3 lb./in, and a wet dry ratio of 27.6%.

5 Example 2

A resin bed was prepared as described in Example 1 using Amberlyst® A-21.

A sample of Cascamid® containing about 7.8 ppm of epichlorohydrin, about 10,800 ppm of dichloropropanol and 114 ppm of chloropropanediol was treated with this bed. A treated sample contained less than 1 ppm of epichlorohydrin, less than 2 ppm of dichloropropanol and about 4.5 ppm of chloropropanediol. Paper treated with the untreated Cascamid® had a wet strength of 12.8 lb./in, a dry strength of 42.1 lb./in, and a wet/dry ratio of 30.4%. Paper treated with the treated sample of Cascamid® had a wet strength of 15.5 lb./in, a dry strength of 45.3 lb./in and a wet/dry ratio of 34.2%.

15 Example 3

A slurry was prepared from 90 g (dry weight) Ambersorb® 563 and 150 ml methanol, was stirred for 30 minutes until the adsorbent sank to the bottom of the mixture and was then loaded to a 1 inch diameter glass column. Excess methanol was drained and the bed was washed with 10 bed volumes of deionized water to remove methanol. The bed was further treated by water backwashing with 100% bed expansion for 30 minutes at 30 ml/minute. Bed volume was approximately 150 ml.

A 12.5% aqueous solution of polyamide paper resin, Cascamid® C-12 containing a total of 6946 ppm of epichlorohydrin, dichloropropanol and chloropropanediol was then passed through the bed at 10 ml/minute by a peristaltic pump. Fractions were collected at 100 ml intervals and analyzed for total epichlorohydrin, dichloropropanol, and chloropropanediol.

	FRACTION, ml	TOTAL, ppm
30	100	< 5
	200	< 5
	300	< 5
	400	< 5
	500	< 5
35	600	< 5
	700	< 5

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	800	< 5
	900	< 5
	1000	< 5
	1100	12
5	1200	55
	1300	240
	1400	616
	1500	1547
10	1600	2568

CLAIMS:

1. A process for increasing the strength of paper and lowering the amount of epichlorohydrin and related hydrolysis compounds that are contained in paper containing polyamide-epichlorohydrin strength enhancing resin, which  
5 comprises adsorbing epichlorohydrin and related hydrolysis compounds contained in an aqueous solution of polyamide-epichlorohydrin resin by contacting the aqueous solution with an adsorbent selected from the group consisting of ion exchange resins, non-ionic polymeric resins, synthetic carbonaceous adsorbents, activated carbon, zeolites, silica, clays, and alumina, and then using the resulting  
10 solution as an additive in the manufacture of paper products.
2. The process of claim 1 in which the aqueous solution is passed through a bed of the adsorbent.
3. The process of claim 2 in which the aqueous solution is contacted with the adsorbent at about room temperature.
- 15 4. The process of claim 3 in which the aqueous solution is about 10 to 35 % by weight resin.
5. A process for lowering the amount of epichlorohydrin and related hydrolysis compounds that are contained in an aqueous solution of polyamide-epichlorohydrin resin, which comprises adsorbing epichlorohydrin and related  
20 hydrolysis compounds contained in an aqueous solution of polyamide-epichlorohydrin resin by contacting the aqueous solution with an adsorbent selected from the group consisting of ion exchange resins, non-ionic polymeric resins, synthetic carbonaceous adsorbents, activated carbon, zeolites, silica, clays, and alumina.

## INTERNATIONAL SEARCH REPORT

PCT/US 93/03431

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D21H17/55		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	D21H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
	No relevant documents disclosed -----	
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
19 JULY 1993		30.07.93
International Searching Authority		Signature of Authorized Officer
EUR PEAN PATENT OFFICE		FOUQUIER J.